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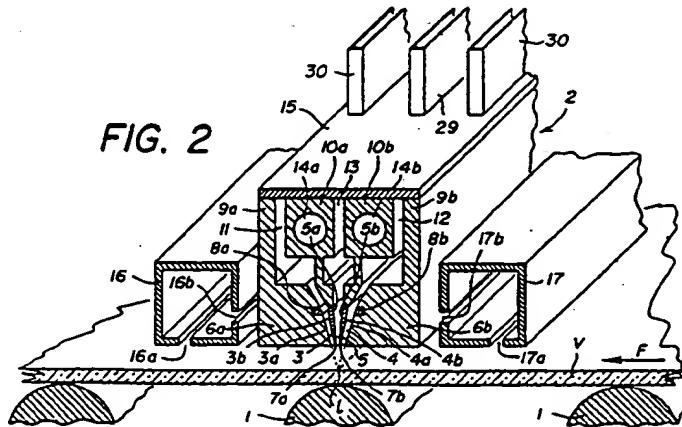
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(54) Process for continuously depositing a layer of a solid material on the surface of a substrate heated to a high temperature and installation for carrying out said process

(57) By means of the nozzle (2), three gaseous curtains are formed converging on the surface of the substrate (V) heated to a temperature of about 600°C which is driven in translatory movement (F), the intermediate curtain being constituted by a gaseous reactant or a

reactant diluted in a carrier gas and the two lateral curtains being constituted by another naturally gaseous reactant or reactant diluted in a gas. The gaseous products of the reaction issuing from the nozzle are compelled to flow above a predetermined region of the substrate and these products are evacuated by suction by means of channels (16, 17) disposed at the extremities of this region of the substrate and a pump (19) to which the channels are connected.

FIG. 2



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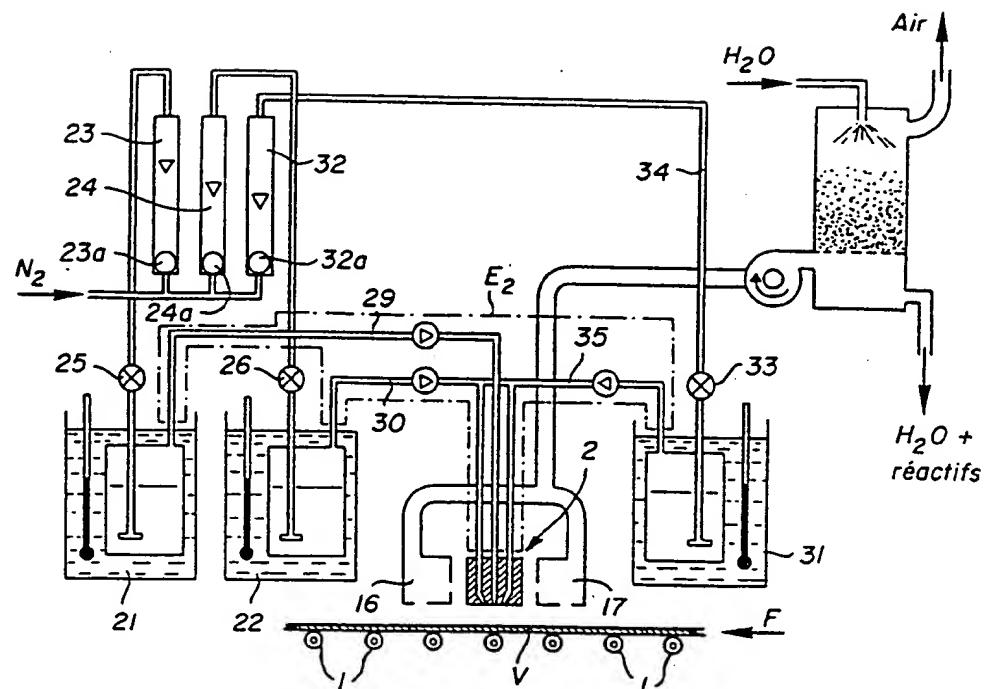


FIG. 1a

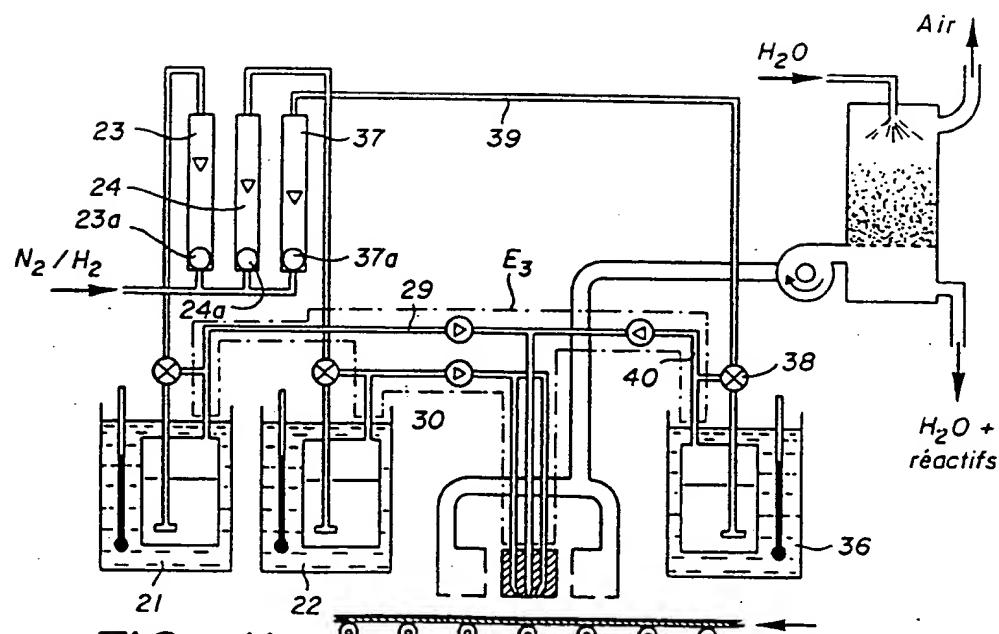


FIG. 1b

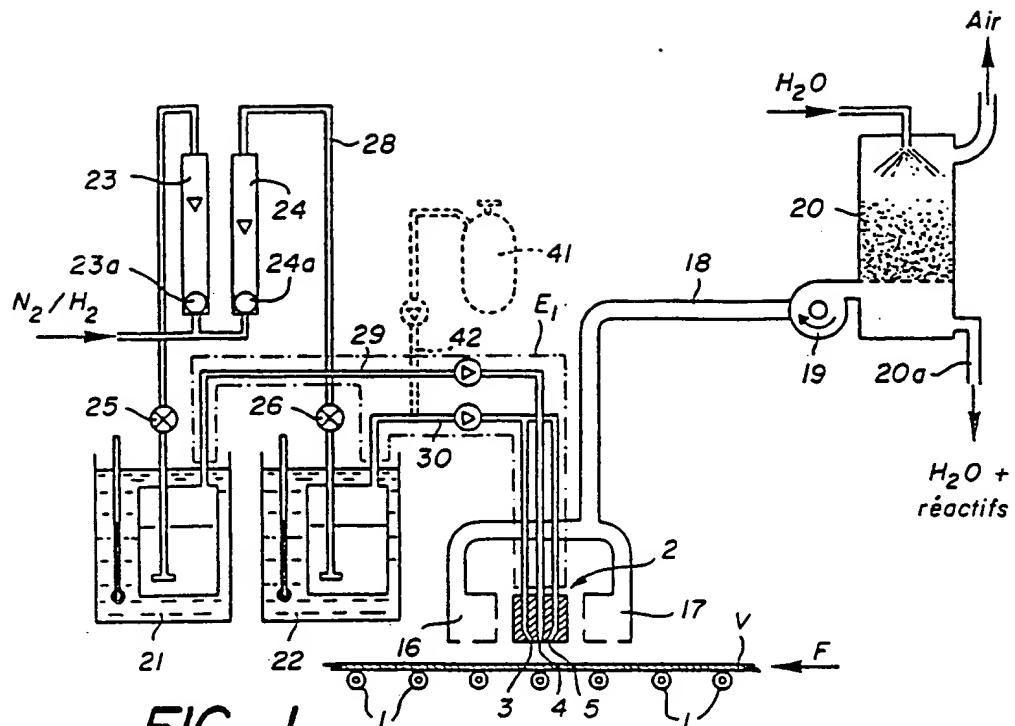


FIG. 1

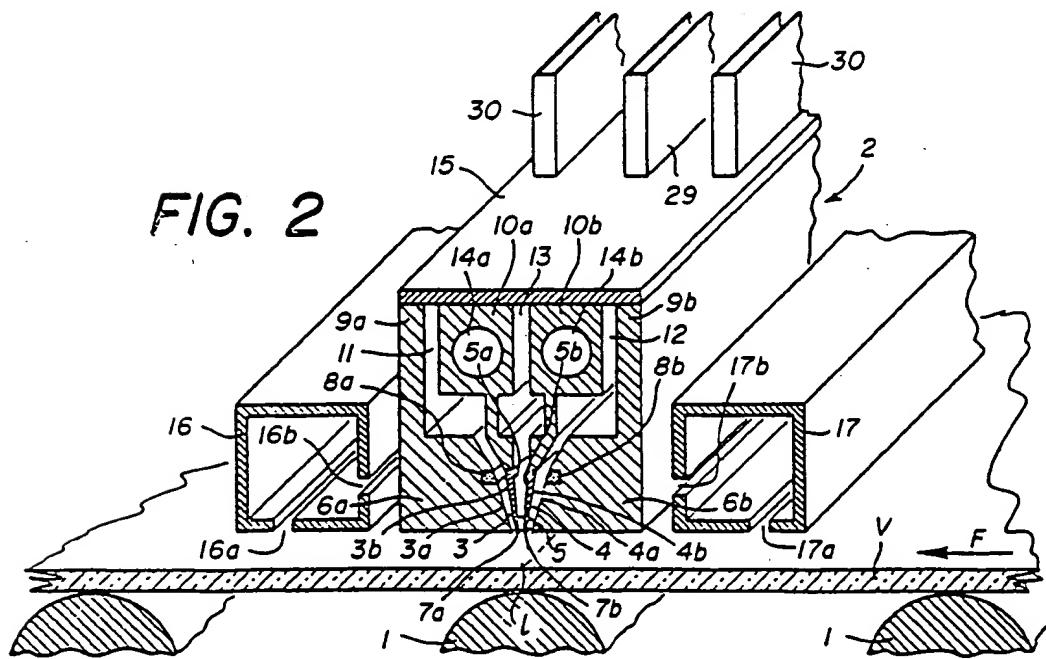


FIG. 2

SPECIFICATION

Process for continuously depositing a layer of a solid material on the surface of a substrate heated to a high temperature and installation for carrying out said process

Various process and devices have already been proposed for coating a substrate, for example a glass plate, with a layer of a semiconductor material, for example tin oxide, which layer must at the same time have a transparency rather similar to that of the substrate, a relatively low electrical resistivity and a high mechanical strength.

Thus, among other processes, it has been attempted in particular to make use for this purpose of the method known under the English designation Chemical Vapor Deposition or C.V.D. More particularly, from the paper by H. Koch entitled: "Elektrische Untersuchungen an Zinndioxydschichten" ("Electrical Investigations on Stannic Oxide Layers) (see Phys. Stat. 1963, Vol. 3, pages 1059 and following a process and a device are known for depositing a thin layer of SnO_2 on a glass plate by reacting SnCl_4 and H_2O supplied in diluted form in a carrier gas, in this case air, and brought in mutual contact with the surface of the glass plate previously heated to a temperature of the order of 200 to 400°C. These two gaseous reactants are projected on the glass by means of a nozzle with two coaxial jet ducts, the central duct of which carries the gaseous dilution of SnO_2 , whilst the outer duct is fed with the gaseous dilution of H_2O .

A process and an apparatus very similar to the foregoing have also been proposed, in particular in German Patent Application No. 2,123,274, published prior to examination, which in addition makes possible doping with antimony of the SnO_2 -layer deposited on a substrate, in this case also a glass plate, in order to reduce the electrical resistivity of this layer. To this end, there was employed in addition SbCl_3 in dilution in a carrier gas, in this case nitrogen, which was brought into contact with SnCl_4 and H_2O above the substrate, by means of a nozzle with three coaxial jet ducts each receiving one of the above components. The combining reaction is thus effected in proximity to the substrate and at a certain distance from the three jet ducts of the nozzle.

In both of the above-cited cases, the processes and devices concerned are designed solely for coating with a doped or undoped SnO_2 -layer platelets of relatively small dimensions on which this coating is effected by relative longitudinal displacement of the nozzle and the platelets. The deposit obtained therefore has the form of a stannic oxide strip of rather uneven transparency over the length of this strip. In fact, the mixture of the reactants emerging from a nozzle of the type described is not perfectly homogeneous, so that the deposit obtained has regions of differing thickness and composition in the form of streaks extending parallel to the axis of relative movement executed by the nozzle and the substrate.

It is opportune to note here that, even if the processes and devices described above are acceptable where it is a matter of coating substrates of

relatively small dimensions, they prove to be practically unusable where a large-scale industrial operation is concerned, relating to the coating of particularly large substrates, as is for example the case of practically endless strips of glass, which may have a width of several metres, such as those obtained by the so-called "float" process.

Indeed, if it were intended to employ for such an application the aforesaid processes and devices, it would be necessary either to dispose side by side, over the entire width of the glass strip, a plurality of the nozzles of the type described, and it is easy to imagine the complexity of the installation which would be involved, or to employ only a limited number of nozzles which a mechanism would have to drive above the strip in a very rapid alternating movement transverse to the axis of movement of the strip to ensure the coating of the whole of the strip surface. It is obvious that neither of these solutions would allow to obtain a SnO_2 -coating sufficiently homogeneous to offer at the same time low electrical conductivity, the transparency and the general high-quality aspect desired in the finished product. If, for example, the latter is a glass intended for use either

in the manufacture of windows or doors of buildings or of windows or windscreens of vehicles of all kinds, it is easily understood that such qualities are highly desirable.

To these should be added further the ability of the desired SnO_2 layers of not impeding the mechanical or thermal treatment to which the glass sheets are usually subjected. In particular, it is necessary that such sheets of glass, coated with doped or undoped SnO_2 , may be cut with diamond by acting on one

face or the other, without impairing the qualities of the SnO_2 -layer. Similarly, it would be necessary to have the facility of subjecting the glass sheets obtained by cutting to a tempering operation, without mechanical or optical deterioration of its coating.

Lastly, it would be desirable to be able to effect the warm bending of such sheets, especially in the manufacture of windscreens or rear windows of cars, for example, again without modifying the previously mentioned qualities of low electrical resistivity, good mechanical properties, good transparency and a light reflection as homogeneous as possible over the entire area of the sheets.

The totality of these requirements cannot be satisfied by using the processes or devices of the described type, that is to say, those which allow to treat individually only a very small glass surface.

It is probable that concerns of the aforesaid nature have led to the replacement of the processes and devices described by those processes and devices which are in particular the subject matter of U.S. Patents Nos. 3,850,679 and 3,888,649, and of British Patent No. 1,507,996.

In these publications as a whole, there is employed generally a device for distributing the previously prepared reactive gases in which these gases are directed at the surface of the glass sheet simultaneously over the entire width of this sheet, in the form of two successive curtains as in the first two Patents, and in the form of a gas stream oriented tangentially to the glass over a preset length of the

sheet, in the third Patent.

However, these devices cannot be suitable for the application of the C.V.D. processes mentioned previously, designed for the deposition of doped or 5 undoped SnO_2 -layers, because the arrival of a gaseous mixture of SnCl_4 and H_2O in proximity of the distributor orifice of these devices would lead to a premature and violent reaction of these components, taking into account the relatively high temperature, practically the same as that of the glass to be coated (of the order of 400°C), of the walls of the devices defining this orifice. Owing to this, two 10 additional drawbacks would result, namely, on one hand, a more or less extensive clogging of the exhaust orifice of the distributor devices and, on the other hand, the formation on the glass of a particularly inhomogeneous SnO_2 -deposit, with the attendant greatly differing electrical, mechanical or physical properties.

20 The purpose of the present invention is precisely to provide a process for continuously depositing on the surface of a substrate heated to a high temperature a layer of a solid material resulting from the reaction of at least two gaseous reactants or reactants diluted in a gas, and an installation for carrying 25 out such a process, which make it possible to avoid all the drawbacks and defects mentioned above.

The process is characterised in that the said streams have the form of rectilinear gas curtains, the 30 transverse profile of each converging toward an imaginary edge common to all streams, that these curtains and/or the substrate are disposed in such a manner that said edge is contained substantially in the plane of the said surface of the substrate, that the 35 gases evolving from the reaction which results from the impact of said streams on the substrate are compelled to flow above a predetermined portion of this substrate extending on either side of said edge and, lastly, that these gases are evacuated at the 40 extremity of said substrate portion located opposite the said imaginary common edge of said curtains.

In a particular mode of execution of this process, the gaseous curtains are three in number in tangential contact by pairs, the central curtain being formed 45 by the stream of the first reactant and the two lateral curtains by the stream of the other reactant.

When this process is applied to deposit on a substrate, in particular a sheet of glass heated to high temperature, of the order of 600°C for example, 50 a layer of SnO_2 by reaction of liquid SnCl_4 and H_2O -vapour diluted in an inert carrier gas, such as nitrogen, the central gaseous curtain will be constituted by the gaseous dilution of SnCl_4 , the two lateral curtains being formed by the dilution of water 55 vapour.

The other subject of the present invention is constituted by an installation for carrying out the described process, installation characterised in that it comprises 60 - a source for a first gaseous reactant or reactant diluted in a carrier gas,
- a source for a second gaseous reactant or reactant diluted in a carrier gas,
- a nozzle with three jet ducts each having an 65 aperture constituted by a rectilinear slot and in

which the lateral walls delimiting the longitudinal edges of each slot converge toward a line common to all jet ducts, a first among these jet ducts adjoining, with a first longitudinal edge of its 70 exhaust aperture, a longitudinal exhaust aperture edge of a second jet duct and, with the second longitudinal edge of said aperture, a longitudinal edge of the exhaust aperture of the third jet duct, -a first and second deflecting surfaces, extending 75 over a predetermined length to each side of said jet ducts from the second longitudinal edge of the exhaust aperture of the second and third jet duct respectively, said deflecting surfaces being coplanar with each other and with the longitudinal edges of 80 the jet duct apertures of the nozzle and being kinematically integral with this nozzle,
- a first distributor network connecting the source of the first reactant with the first jet duct of the nozzle,
- a second distributor network connecting the source 85 of the second reactant with the second and third jet duct of the nozzle,
- means for setting in relative movement the substrate and the nozzle in a direction substantially perpendicular to said imaginary line,
90 - means for maintaining constant in the course of said relative movement the distance separating the plane containing said jet duct apertures of the nozzle and said deflecting surfaces from the said surface of the substrate, this distance being substantially equal 95 to that comprised between the jet ducts of the nozzle and the said imaginary line,
- at least one device for evacuating the reaction gases evolving in the space comprised between said deflecting surfaces and the surface of the substrate,
100 from the extremities of this space most remote from the apertures of said nozzles.

As will be seen in the following, the above process and installation make it effectively possible to carry out the coating, at a very high speed, of sheet or plate glass, with an SnO_2 -layer of excellent homogeneity, guaranteeing very high performance levels with respect of mechanical qualities and of electrical and optical properties of all kinds.

The attached drawing shows, by way of example 110 and very schematically, a form of embodiment of the installation being the subject of the present invention:

Figure 1 is a general view.

Figures 1a and *1b* are views similar to that of 115 *Figure 1*, in accordance with modified forms of embodiment.

Figure 2 is a partial perspective view, in vertical section on an enlarged scale, of an element of the installation in *Figure 1*.

120 The installation shown in the drawing is designed to deposit by the so-called C.V.D.-method on a substrate, in this case a sheet of glass V heated to high temperature, a layer of stannic oxide SnO_2 , by exploiting the following chemical reaction:



To this end, the installation comprises first of all a train of rollers 1 on which the sheet V rests and 130 moves in direction F, which rollers are driven in

anti-clockwise rotation by an electric motor (not shown) and which have, of course, a length compatible with the width of the sheet of glass to be carried. The speed of rotation of the rollers 1 will be so selected that the displacement of the sheet V is effected with a linear speed of some metres per minute, of the order of 1 to 10, according to each case.

Above this train of rollers 1, the installation shown has a nozzle 2, the basic structural profile of which is the subject of figure 2, to which reference will be made from now on. This nozzle comprises in fact three separate jet ducts 3, 4 and 5, respectively, extending longitudinally in a direction parallel to the already mentioned rollers 1, over a length corresponding to the width of the glass sheet V. Thus, such jet ducts could have a length of several metres. As can be seen in the drawing, the jet ducts 3 to 5 are formed by assembly of elongated sectional shapes 6a and 6b, 7a and 7b, 8a and 8b, which are in turn fastened, by any suitable means, to two pairs of profiled elements 9a and 9b, 10a and 10b, respectively, delimiting between each other ducts 11, 12 and 13 communicating with the jet ducts 3, 4 and 5, respectively.

The lateral walls 3a and 3b, 4a and 4b, 5a and 5b of the jet ducts 3 to 5 converge toward a common line ℓ located at a distance from the plane containing the inner face of the sections 6a and 6b of the order of 30 to 6 mm, for example. Furthermore, the exhaust apertures of the blast pipes 3, 4 and 5, which are in the shape of three oblong slots extending over the entire length of the sections 6a, 7a, 7b and 6b, have a width of some tenths of a millimetre, for example 1/10 or 2/10.

The width of the lower face of sections 6a and 6b will be preferably comprised between 10 and 20 times the total width of the exhaust slots of jet ducts 3 to 5.

Preferably, but not exclusively, this lower face of sections 6a and 6b will be covered with a layer of a chemically inert metal or an alloy of such metals or again of metal oxides. By way of example, the metal could be gold or platinum. The oxides could be selected among SnO_2 , SiO_2 or Al_2O_3 .

In fact, the usual metals and alloys, such as steel or brass have, in the presence of hydrogen, catalytic properties which could perturb the control of the desired reaction to obtain a deposit of SnO_2 having the desired mechanical, physical and optical qualities. The reason for the presence of hydrogen will be explained in the following.

It is of course understood that the assembly of the sections constituting the nozzle 2 is covered, at each extremity, by a cover plate, not shown, mounted so as to ensure total fluid-tightness and to form in this manner the jet ducts 3, 4 and 5 and the ducts 11, 12 and 13 which are to be well sealed laterally. The channels 14a and 14b formed in the upper part of sections 10a and 10b, over the entire length of the latter, make it possible to establish a circulation of a fluid, for example oil, intended to maintain the nozzle 2 at an optimum operating temperature.

Another plate 15 covers the upper face of nozzle 2 over its whole area and in a fluid-tight manner, thus

preventing any communication between the ducts 11, 12 and 13.

It will be noted further that the general profile and the surface quality of the walls delimiting not only the jet ducts 3 to 5 but also the ducts 11 to 13 as well as the transverse sections of the latter are such, that for gas flow rates of the order of 3 to 6 l/h per centimetre of nozzle length the flow at the outlet of the nozzles will be of "laminar" type.

To either side of the nozzle 2, and over the entire length of the latter, the installation shown comprises two suction channels 16 and 17 (Figure 1 and 2), of straight square section and the lower face of which is coplanar with the lower face of the sections 6a and 8b previously described. These channels each have two longitudinal slits, 16a and 16b for channel 16, 17a and 17b for channel 17, respectively. These channels are connected, by a conduit system 18, to the intake of a suction pump 19 connected, with its outlet, to the bottom of a scrubbing tower 20 filled with refractory materials (Raschig rings).

In addition, the installation shown comprises two thermostat-controlled bubble tanks 21 and 22, the first containing liquid stannic chloride, SnCl_4 , and the other water, two flowmeters 23 and 24 having a flow-regulating valve, 23a and 24a, fed with a mixture of nitrogen and hydrogen in 60/40 ratio, two valves 25 and 26 fitted on the pipes 27 and 28 connecting the flowmeters to the bubble tanks 21 and 22 mentioned above. Two conduits 29 and 30 connect the outlet of the vessels 21 and 22 respectively to the duct 13 and to the ducts 11 and 12 of the nozzle 2, that is to say, in fact to the jet duct 5 of this nozzle, for the conduit 29, and to the jet ducts 3 and 4, for the conduit 30.

The conduits 29 and 30 pass through an enclosure E_1 , illustrated schematically by a contour drawn in composite lines, containing a heating liquid, for example oil, maintained at a constant temperature of about 110°C by any suitable means.

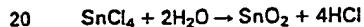
The installation described in the foregoing makes it possible to coat, for example, a glass plate with a layer of stannic oxide having a thickness of the order of 500 nm, having at the same time a very good transparency, a relatively low electrical conductivity and a high mechanical strength and resistance to acids.

An experimental installation of this type, fitted with a 20 cm long nozzle in which the aperture of the jet ducts 3, 4 and 5 had a width of 0.1 - 0.1 and 0.2 mm, allowed to treat a glass plate of 20 cm width and 4 mm thickness heated to about 600°C and driven in the direction F (Figure 1 and 2) with a velocity of 2 m/min. The distance separating the lower face of the nozzle and the surface of the glass was 6 mm.

The vessels 21 and 22 employed had respective capacities of 200 ml for liquid SnCl_4 and 300 ml for H_2O . These vessels were heated to such temperatures that, for a carrier gas flow rate of 60 l/h N_2H_2 for vessel 21 and 120 l/h for vessel 22, the flow rates being controlled by operation of valves 23a and 24a, there was obtained a flow rate of reactant diluted in this gas of 2 mol/h stannic chloride, SnCl_4 and 1 mol/h H_2O . In addition, the temperature of the nozzle

was maintained at approximately 110°C by circulation of the oil in the channels 14a and 14b of the latter (Figure 2).

Taking into account the profile given to the jet ducts 3, 4 and 5 of nozzle 2, and in particular the fact that they converge with their lateral walls toward a common line *l*, the gaseous streams which issue from these mouthpieces, SnCl_4 -stream from jet duct 5, and H_2O -vapour from jet ducts 3 and 4, which are laminar, enter into mutual contact firstly by touching each other tangentially then more and more directly as the line "l" is approached. Of course, the combined flow of these three gaseous streams becomes less and less laminar in the measure as these three streams interpenetrate. However, the latter takes place in fact only in the immediate proximity of the surface of the glass *V*, which, as stated, is heated to about 600°C, so that the combining reaction



occurs on the glass. It is opportune to remark at this point that, if no particular measures were taken, this reaction would occur in a very violent manner with production of a very large quantity of stannic oxide SnO_2 and of hydrates of the type $\text{SnO}_2 \cdot \text{H}_2\text{O}$ at the outlet of the jet ducts 3 to 5 of nozzle 2, with the risk of partial or total clogging of the jet ducts, and a deposition of these same oxides on the glass in the form of a white precipitate and not in the form of the desired transparent semiconductor layer.

With the above-described installation, this risk was eliminated by adding a reducing agent to the gaseous streams of SnCl_4 and H_2O -vapour in the form of H_2 , incorporated into the carrier gas. Hydrogen does in fact not react with either SnCl_4 or H_2O . Moreover, it acts as a catalyst. It can therefore be used as an inert carrier gas.

The combining reaction of SnCl_4 and H_2O occurs not only in the central region of the nozzle 2, that is to say in proximity to that part of this nozzle into which open the jet ducts 3, 4 and 5. In fact, this reaction takes place when the pump 19 operates in such a manner, that, by the channels 16 and 17 disposed to either side of the nozzle, there is formed an underpressure at the right-hand and left-hand extremities, in the drawing, of the space comprised between the glass plate *V* and the lower face of sections 6a and 6b of the nozzle. Owing to this, there is formed in this space a gas flow moving from the central portion of this space towards the channels 16 and 17 already mentioned. This stream contains above all a portion of the SnCl_4 and H_2O dispersed in the carrier gas and as yet unreacted, the already formed HCl -vapours, and a certain quantity of carrier gas free from the reactants which have already reacted. Thus, the reaction between SnO_2 and H_2O can continue with the residual reactant gases over a certain length, to either side of the line "l" of convergence of the jet ducts.

The power of the suction realized with the channels 16 and 17 is selected in such a manner that the reactive gases issuing from the nozzle 2 do not reside in this space longer than the time strictly necessary for obtaining a deposit of SnO_2 on the

glass, which deposit appears in the form of a transparent layer and not in the form of an accumulation of powdery SnO_2 . Of course, the suction must not be too strong, because otherwise the reactive gases issuing from the nozzle would not have the time to reach the surface of the glass. The intensity of the suction is therefore of critical importance with regard to the quality and the rate of growth of the layer. It will be noted in addition that, by means of this suction, in a manner of speaking the space comprised between the nozzle and the glass plate, in which space the desired reaction takes place, is insulated from the ambient atmosphere, preventing, on the one hand, any possible penetration into this space of additional moisture capable of influencing the combination reaction whilst preventing, on the other hand, any leakage to this same ambient atmosphere of noxious vapours, for example HCl or hydrogen, the ambient air tending to flow towards the slots 16a and 16b, 17a, 17b, respectively, passing between the channels 16 and 17 respectively, the glass plate *V* and the nozzle 2.

The gaseous products drawn off by pump 19 are directed, as stated, to the scrubbing tower 20, so that the residual volatile acids percolate and are entrained by the water, the resulting acid solution being separated from the scrubbed gases and evacuated through the conduit 20a.

With the operating conditions described above, the reaction yield was about 70%. The glass was coated over the whole of its surface with a SnO_2 -layer, having a thickness of 500 nm, a transparency of 90 to 95% according to sample and a mean conductivity $R = 200 \Omega$. Moreover, the SnO_2 -layer thus obtained was found to be of a particularly high hardness, greater than that of the glass on which it has been deposited. Accordingly, it has a great resistance, be it to the most intense mechanical stresses, for example to impact, or to acids. In particular, this glass could be subjected to a bending operation with a radius of curvature of 15 cm, after being heated to a temperature between 600 and 700°C, without any deterioration in the SnO_2 -coating. It was also possible to temper it under the usual conditions applying to conventional glass. Lastly, it is to be noted that a glass plate coated with a SnO_2 -layer in the conditions and by the method described, can be cut with diamond on either face without splintering of the coating.

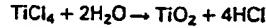
With the same installation, and operating conditions differing from those indicated only in the velocity of advance of the plate *V*, this velocity having been raised to approximately 10 m/min, there was obtained an SnO_2 deposit having a thickness of approximately 10 nm, a mean conductivity $R = 1.5 \text{ K}\Omega$, a transparency of almost 100 % for visible radiation and mechanical properties practically equivalent to those of the layer obtained by advancing the glass plate at a speed of 2 m/min.

The installation described in the foregoing can also be employed to deposit, by C.V.D., a layer of TiO_2 on a glass plate. To this end, it suffices to replace in the bubble tank 21 the stannic chloride SnCl_4 with titanium tetrachloride TiCl_4 . It would also

be possible to employ a carrier gas constituted solely by nitrogen.

The reaction which will take place at the outlet of nozzle 2 will be as follows:

5



A glass plate of 20 cm width and 4 mm thickness, heated to a temperature of 600°C, was displaced 10 longitudinally at a rate of 2 m/min in front of a nozzle 2, at a distance of 6 mm from the latter. By operating the valves 23a and 24a, the flow rate of the carrier gas was adjusted to 60 1/h for the flowmeter 23 and to 120 1/h for the flowmeter 24. In addition, the 15 vessels 21 and 22 were heated to achieve reactant flow rates of 0.2 mole/h TiCl_4 and 0.01 mole/h H_2O .

There was obtained a TiO_2 layer of 0.01 μm thickness, having a transparency of about 75% to visible light and a reflecting power for this same 20 visible light of the order of 50%, that is to say, greater than the glass bearing the deposit. The mechanical strength was comparable to that of a SnO_2 -layer obtained in the manner described.

The direct addition of H_2 , in order to attenuate the 25 violence of the combination reaction between SnCl_4 and H_2O -vapour, is not the only possible measure. According to a modified mode of execution of the process according to the invention, it is possible to make use of a carrier gas constituted exclusively by 30 nitrogen and to produce *in situ* the hydrogen necessary for the reduction, from methanol, CH_3OH . Figure 1a shows how the installation already described (Figure 1) is to be modified in this case.

As shown, the new installation must comprise an 35 additional bubble tank 31, containing the methanol, a flowmeter 32 with its flow-control valve 32a, a valve 33 located on a pipe 34 connecting the flowmeter 32 to the vessel 31 and lastly a conduit 35, connecting the outlet of this vessel to the conduit 30 40 and thus, to the ducts 11 and 12 of nozzle 2, and thereby to the outer jet ducts 3 and 4 of the latter.

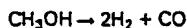
The conduits 29, 30 and 35 pass through an enclosure E_2 , indicated schematically by a contour drawn in composite lines, containing a heating 45 liquid, for example oil, kept at a constant temperature of about 110°C in any suitable manner.

When brought into the presence of SnCl_4 , the methanol can react with the latter in the following manner:

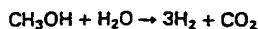
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Furthermore, taking into account the relatively high temperature prevailing at the outlet of the jet 55 ducts, the methanol can decompose according to the reaction

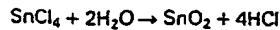


60 It can also react with H_2O according to the reaction:



65 In either case, there is thus ensured the *in situ*

production of the hydrogen necessary for controlling the already mentioned essential reaction:



70

It is opportune to remark that the experiments have not permitted to determine which of the three above reactions of CH_3OH had precedence. It has nevertheless been noted that, in the operating 75 conditions described in the following, the introduction of methanol into the process of depositing the desired SnO_2 layer effectively made it possible to control this process in the same manner as in the case where the hydrogen was mixed to the nitrogen as carrier gas (Figure 1).

To obtain, with the pilot installation already described and modified by the addition of the elements required by this mode of execution, a glass plate of 20 cm width and covered with a transparent SnO_2 -layer, through each of the three vessels 21, 22 and 31 a flow of about 60 1/h nitrogen is passed, all flow rates being controlled by operation of the valves 23a, 24a and 32a with which are equipped the flowmeters 23, 24 and 32. These vessels were heated to suitable 90 temperatures to effect that their flow rates of the corresponding reactant are respectively 1 mole/h of SnCl_4 , 1 mole/h H_2O and 0.5 mole/h CH_3OH . As previously, the temperature of the nozzle, maintained by oil circulation, was 110°C, whilst the glass 95 plate was preheated to a temperature of about 600°C. The glass was driven in the direction F at a velocity of 2 m/min, keeping it at a distance of 6 mm from the lower face of sections 6a and 6b constituting the nozzle.

100 The SnO_2 -coating obtained was found to be practically identical in thickness, quality and mechanical, electrical or physical properties to the similar coating obtained with the aid of the installation illustrated with reference to Figure 1.

105 The variant of the installation which is the subject of Figure 1b is more particularly designed for producing antimony-doped SnO_2 -layers, by replacing certain tin atoms with Sb. It is known in fact that by means of such doping, it is possible in particular 110 to obtain a relatively substantial reduction of the resistivity of the layer.

Such doping can be obtained by carrying out the following reaction:



which makes it possible accessorially to introduce antimony ions into the crystal structure of SnO_2 .

120 Since the antimony chloride reacts with water but not with stannic chloride, the installation according to Figure 1b is embodied in such a manner that the SbCl_5 only comes into contact with H_2O at the outlet of nozzle 2, whilst being mixed with stannic chloride, SnCl_4 . Thus the above reaction takes place simultaneously with that of the combination of SnCl_4 and H_2O -vapour.

125 The new installation differs from that of Figure 1 by the addition of a bubble tank 36, containing the liquid antimony chloride SbCl_5 , a flowmeter 37 with 130 control valve 37a, and lastly a conduit 40 connecting

the outlet of this vessel to conduit 29, and thus to the central jet-duct 5 of the nozzle through the duct 13 of the latter (Figure 2); also, a pipe 39 carries a valve 38.

The conduits 29, 30 and 40 pass through an 5 enclosure E₃, illustrated schematically by a contour drawn in composite lines, containing a heating liquid, for example oil, maintained at a constant temperature of about 110°C in any suitable manner.

A pilot installation of this type, fitted with a nozzle 10 having the same features as those of the nozzle of the pilot installation already described, mounted in accordance with the diagram of Figure 1, made it possible to coat a glass plate of 20 cm width and 4 mm thickness with a deposit of antimony-doped 15 SnO₂ of 500 nm thickness. Essentially, the operating conditions were as follows:

The glass was heated to a temperature of 600°C approximately and was displaced longitudinally at a distance of 6 mm from the nozzle with a velocity of 2 20 m/min. The carrier gas used was a mixture of nitrogen and hydrogen N₂ 40 % H₂ and the flow rates of this gas were adjusted, by operating the valves 23a, 24a and 33a, to the following values : 60 1/h for the vessel 21 containing the liquid SnCl₄, 60 1/h for 25 the vessel 22 containing H₂O and 20 1/h for the vessel 36, containing the liquid SbCl₅. Moreover, the vessels were heated so as to obtain reactant flow rates, respectively, of 2 mole/h SnCl₄, 2 mole/h H₂O and 0.1 mole/h SbCl₅.

30 There was obtained a doped SnO₂ layer having a resistivity R of the order of 70Ω and a transparency of 60 %. The other properties, such as mechanical strength, impact resistance, tear resistance, acid resistance and suitability for thermal treatment such 35 as tempering of the coated glass were equivalent to those of the undoped SnO₂-layers deposited in the manner already described. Its reflecting power was practically the same as that of the glass on which the layer has been deposited.

40 With this same installation and under operating conditions differing from those indicated above only with regard to the speed of advance of the plate V, which velocity was raised to about 10 m/min, there was obtained a deposit of antimony-doped SnO₂ 45 having a thickness of approximately 10 nm, a mean conductivity R = 500Ω, a transparency of 80% in the visible spectrum and mechanical properties identical to those obtained with the similarly antimony-doped SnO₂ deposit covering a glass plate displaced at a 50 speed of 2 m/min.

Although the installation illustrated in Figure 1b employs, by way of reducing agent, hydrogen introduced into the carrier gas, namely nitrogen, it is obvious that it would be equally possible to conceive 55 a similar installation in which the reducing agent would be obtained from methanol, CH₃OH, as in the case of the form of embodiment shown in Figure 1a. Thus, the new installation would be a combination of the installations in Figures 1a and 1b, because it 60 would comprise, in addition to the vessels 21 and 22 containing the SnCl₄ and water, respectively, vessels 31 and 36 containing, respectively, the CH₃OH and the SbCl₅. These vessels would be connected to the nozzle 2 in the same manner as in the assemblies of 65 Figures 1, 1a and 1b. On this assumption, the above

vessels would be fed with nitrogen at flow rates of 60 1/h, with the exception of the vessel for SbCl₅ which would receive only 20 1/h. The heating temperatures of the vessels would be such that the following

70 reactant feed rates to the nozzle 2 would obtain : 1 mole/h for SnCl₄, 1 mole/h for H₂O, 2 mole/h for CH₃OH and 0.1 mole/h for the SbCl₅.

The resistivity, the reflecting power and the transparency of the SnO₂-layers on the glass can be 75 improved to a very great extent if these layers are fluorine-doped layers. To this effect, preferably the installation described with reference to Figure 1 will be used, augmented by a cylinder 41 containing gaseous HF, and by a conduit 42 connecting this cylinder to the conduit 30, the whole being shown in broken lines in the drawing.

A glass of 4 mm thickness, heated to a temperature of about 600°C, was coated with a 900 nm thick layer of SnO₂, doped with fluorine by passing in 80 front of the nozzle at a velocity of 2 m/min and at a distance of 6 mm therefrom. The flow rates of the carrier gas (a mixture of N₂ 40 % H₂) were of 60 1/h for the SbCl₄ and the water vapour. The flow rate of HF was 0.1 1/min.

90 The fluorine-doped SnO₂ coating was found to have particularly high performance. In fact, its resistivity was R = 20Ω, its reflecting power in visible light greater than that of the supporting glass, and its infrared reflecting power was found to be particularly 95 high, of the order of 75%. Moreover, its transparency to visible light was 90 %. Its mechanical strength properties were also very pronounced: the glass coated with fluorine-doped SnO₂ was able to undergo a thermal treatment of tempering identical 100 to those to which are traditionally subjected certain vehicle windows, for example the side windows of automobile vehicles. It was also possible to bend such a plate when hot (temperature approximately 650°C) with curvature radii of 15 cm without modifying the properties of the doped SnO₂ coating.

Moreover, a glass plate coated in the described manner could be worked in the traditional fashion (cutting, grinding, etc....) without damage to the coating. The layer of SnO₂ doped with F had in fact a 110 hardness greater than that of the supporting glass and could not be scratched, while its chemical resistance to acids and its impact resistance were found to be particularly high.

It is to be remarked further that a layer of SnO₂ 115 doped with fluorine or antimony deposited on a plate of glass in the conditions stated can be coated with silver or a silver paint deposited at 600°C, for example in order to form electrical contacts. Such a silver coating adheres very well to the surface of the 120 SnO₂ layer.

With this same installation (Figure 1b) and under operating conditions differing from those indicated above only with respect to the speed of advance of the plate V, this speed having been raised to 125 approximately 10 m/min, there was obtained a fluorine-doped SnO₂ deposit having a thickness of about 10 nm, a mean conductivity of R = 200Ω, a transparency of almost 100 % in the visible spectrum, an infrared-reflecting power of 25 % and 130 mechanical properties identical to those obtained

with the SnO_2 -deposit also doped with fluorine by displacement of the glass plate at a velocity of 2 m/min.

Although the installation shown in Figure 1, 5 augmented by a cylinder 41 containing gaseous HF and by a conduit 42 connecting this cylinder to the conduit 30, uses by way of reducing agent hydrogen introduced into the carrier gas (nitrogen), it is obvious that it would be equally possible to conceive 10 an installation making it possible to obtain fluoroine-doped SnO_2 layers in which the reducing agent would be obtained from methanol, CH_3OH , as in the case of the form of embodiment of the installation illustrated in Figure 1a. This new installation would 15 thus be a combination of the installations of Figures 1 and 1a: it would appear in practice as the installation of Figure 1a with addition of the HF-cylinder 41, connected to the conduit 30 by the conduit 42, all these being elements already described previously with reference to the installation in Figure 1 and illustrated in broken lines in this figure.

On these assumptions, the vessels 21, 22 and 31, 20 would be fed with nitrogen at flow rates of 60 l/h, the flow rate of HF being 0.1 l/h. They would be heated to such temperatures that the flow rates of the reactants transported toward the nozzle 2 would be of 1 mole/h for SnCl_4 , 1 mole/h for H_2O and 2 mole/h for CH_3OH .

30 In the conditions stated above, a glass of 4 mm thickness, heated to a temperature of about 600°C, was coated with a layer of 600 nm of fluorine-doped SnO_2 by passing in front of the nozzle 2 which was maintained at a temperature of approximately 110°C 35 in the previously described manner, at a speed of 2 m/min and at a distance of about 6 mm from this nozzle.

The SnO_2 deposit thus obtained had a resistivity of about $R = 40\Omega$. The other features of physical, 40 optical or mechanical nature remained comparable to the fluorine-doped SnO_2 coating obtained by direct introduction of the hydrogen into the carrier gas (installation in accordance with Figure 1, augmented by cylinder 41).

45 The uses of glass plates of all dimensions coated with a layer of undoped SnO_2 or doped with antimony or fluorine can be of the most diverse kind, depending on their physical and electrical properties in particular.

50 Although an undoped layer of SnO_2 has a relatively high resistivity when compared with the resistivity of a similar layer doped with antimony or fluorine, a glass panel covered with such a layer can be used for example to constitute windows or window-casing 55 for dwellings, ships or trains, in view of its good transparency to visible light and its relatively high infrared-reflecting power. In fact, such a plate has a sufficient athermic capacity to reduce substantially the thermal sunrays likely to pass through this panel.

60 This athermic capacity is obviously greater when a glass coated with antimony-doped SnO_2 or a glass coated with fluorine-doped SnO_2 is concerned.

Moreover, the resistivity of such layers being rather low in the case of antimony-doped SnO_2 and very 65 low in the case of fluorine-doped SnO_2 , it is possible

to employ glasses coated with doped SnO_2 as heating windows, for example as rear windows of cars.

It has moreover been observed that, when placed 70 in a very humid atmosphere, a glass panel carrying a coating of SnO_2 , doped with antimony or fluorine or not, does not cover itself with a uniform layer of mist but rather with a multiplicity of droplets, thus effecting to a much lesser extent the visibility 75 through the coating proper and the glass panel.

The property is obviously very advantageous in the case of glass panels designed to form windows, notably car windows and especially windscreens and rear windows of cars, buses or vans.

80 Although in the preceding description reference was made to the forms of embodiment of installations in which the glass plates to be coated with a layer of SnO_2 , doped or not, are always placed at a distance from the nozzle corresponding to the 85 distance separating this nozzle and the edge of convergence of the lateral walls of the three jet ducts of this nozzle, it will be noted that, in practice, it will be possible to reduce slightly this distance in order to effect that the mixing of the reactants issuing from 90 these blast-pipes takes place on impact on the glass, producing a relatively intense local turbulence which promotes this mixing.

Lastly, it will be noted that, although mentioned within the scope of the process and of the installations described with reference to Figures 1, 1a, 1b and 2, of the attached drawings, the use of hydrogen as a means for controlling the combination reaction of SnCl_4 and H_2O could also take place, for the same purposes and with the same benefits, if such a 100 reaction were obtained by employing processes and installations of different nature functioning in accordance with the C.V.D. method, such as those described by H. Koch in the previously cited paper or in the German Patent Application No. 2 123 274 105 published prior to examination.

CLAIMS

1. A process for continuously depositing on the surface of a substrate heated to high temperature a layer of a solid material resulting from the reaction of at least two gaseous reactants or reactants diluted in a gas, in which method discrete laminar streams of each reactant are formed and in which these 110 streams are projected on said substrate by bringing the streams together in reciprocal tangential contact while said streams and the substrate are displaced relatively in such a manner that said streams are applied successively to different regions of the substrate, and in which method said streams have the form of rectilinear gas curtains, the transverse profile of each converging towards an imaginary edge common to all streams, these curtains and/or the substrate are disposed in such a manner that 115 120 said edge is substantially in the plane of the said surface of the substrate, the gases evolving from the reaction which results from the impact of said streams on the substrate are compelled to flow above a predetermined portion of this substrate 125 130 extending on each side of said edge, and these gases

are evacuated at the extremity of said substrate portion located opposite the said imaginary common edge of said curtains.

2. A process according to claim 1, characterised in that the said gaseous curtains are at least three in number and are disposed one beside the other in tangential contact by pairs, and the intermediate curtain is constituted by the flow of the first reactant whilst the lateral curtains are formed by the gaseous flow of the other reactant.

3. A process according to claim 2, for depositing a layer of SnO_2 by reaction of SnCl_4 and water vapour, diluted in inert carrier gas, or depositing a layer of TiO_2 by reaction of TiCl_4 and water vapour, diluted in inert carrier gas, and in which the dilute stream of SnCl_4 , or of TiCl_4 , constitutes the intermediate curtain, and the lateral curtains are formed by the diluted water vapour.

4. A process according to claim 3, in which the first reactant is SnCl_4 , and an additional reactant, in the form of SbCl_5 diluted in an inert gas, is added to the diluted SnCl_4 prior to forming the said intermediate gaseous curtain, whereby the said layer is antimony-doped SnO_2 .

5. A process according to claim 3, in which the first reactant is SnCl_4 , and an additional reactant constituted by gaseous HF is added to the said diluted water vapour prior to forming the said lateral curtains, whereby the said layer is fluorine-doped SnO_2 .

6. A process according to claim 3, 4, or 5 in which, for attenuating the reaction, SnCl_4 and the water vapour are reacted in the presence of a reducing agent.

7. A process according to claim 6, characterised in that the said reducing agent is formed in situ, from methanol, CH_3OH , introduced into the diluted water vapour.

8. A process according to claim 6, characterised in that the said carrier gas is formed by a mixture of nitrogen and hydrogen, the hydrogen constituting the said reducing agent.

9. A process according to claim 8, characterised in that the carrier gas is formed of 60% nitrogen and 40% hydrogen.

10. Apparatus for continuously depositing on the surface of a heated substrate a layer of solid material formed from the reaction of at least two reactants selected from gaseous reactants and reactants diluted in inert carrier gas, which apparatus comprises: a source of a first gaseous reactant or reactant diluted in a carrier gas, a source of a second gaseous reactant or reactant diluted in a carrier gas, a nozzle with three jet ducts each having an exhaust aperture constituted by a rectilinear slot and in which the lateral walls delimiting the longitudinal edges of each slot converge towards a line common to all said jet ducts, a first of these jet ducts adjoining, with a first longitudinal edge of its exhaust aperture, a longitudinal exhaust aperture edge of a second jet duct and, with the second longitudinal edge of said aperture, a longitudinal edge of the exhaust aperture of the third jet duct, first and second deflecting surfaces, extending over a predetermined length to each side of said jet ducts from the second longitudinal edge of the exhaust aperture of the second and third jet ducts respectively, said deflecting surfaces being coplanar with each other and with the longitudinal edges of the exhaust apertures and being kinematically integral with this nozzle, a first distributor network connecting the source of the first reactant with the first jet duct of the nozzle, a second distributor network connecting the source of the second reactant with the second and third jet ducts of the nozzle, means for setting in relative movement the substrate and the nozzle in a direction substantially perpendicular to said imaginary line, means for maintaining constant in the course of said relative movement the distance separating the plane containing said exhaust apertures of the nozzle and said deflecting surfaces from the said surface of the substrate, this distance being substantially equal to that between the jet ducts of the nozzle and the said imaginary line, and at least one device for evacuating the reaction gases evolving in the space between the said deflecting surfaces and the surface of the substrate, from the extremities of this space most remote from the exhaust apertures.

11. Apparatus according to claim 12, characterised in that the width of the slots constituting the exhaust apertures of the blast-pipes of the nozzle is not less than 1/10 mm and not greater than 2/10 mm.

12. Apparatus according to claim 13, characterised in that the first and second deflecting surfaces extend, to each side of the jet ducts of the nozzle, over a length which is 10 to 20 times greater than the width of the slots constituting the exhaust apertures of the jet ducts.

13. Apparatus according to claim 14, characterised in that the distance separating the said deflecting surfaces and the surface of the substrate is between 3 and 6 mm.

14. Apparatus according to any one of claims 12 to 15 characterised in that the first and second deflecting surfaces are covered with a layer of a chemically inert metal or an alloy of such metals.

15. Apparatus according to any one of claims 12 to 15 characterised in that the first and second deflecting surfaces are covered with a layer of a chemically inert metal oxide.

16. Apparatus for coating a substrate, substantially as herein described with reference to Figures 1 and 2, Figure 1a or Figure 1b of the accompanying drawings.

17. A method of coating a substrate, as claimed in claim 1 and substantially as herein described.

18. A substrate when coated by the method or apparatus claimed in any one of the preceding claims.

120

New claims or amendments to claims filed on 1.7.80
Superseded claims 1
New or amended claims:-

125 1. A process for continuously depositing on the surface of a substrate heated to high temperature a layer of a solid material resulting from the reaction of at least two gaseous reactants or reactants diluted in a gas, in which method discrete laminar streams of each reactant are formed and in which these

streams are projected on said substrate by bringing the streams together in reciprocal tangential contact while said streams and the substrate are displaced relatively in such a manner that said streams are 5 applied successively to different regions of the substrate, and in which method said streams have the form of rectilinear gas curtains, the transverse profile of each converging towards an imaginary edge common to all streams, these curtains and/or 10 the substrate are disposed in such a manner that said edge is substantially in the plane of the said surface of the substrate, that the said substrate and said curtains are displaced relative to each other in a direction substantially perpendicular to the said 15 common edge in such a manner that the said edge remains substantially in the plane of the said surface of the substrate, the gases evolving from the reaction which results from the impact of said streams on the substrate are compelled to flow above a 20 predetermined portion of this substrate extending on each side of said edge, and these gases are evacuated at the extremity of said substrate portion located opposite the said imaginary common edge of said curtains.

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